



Influence of electrolyte additives on safety and cycle life of rechargeable lithium cells

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Abstract

The influence of electrolyte additives on the safety and cycle life of 4V-class lithium cells is examined. The electrolyte solution employed was 1 M LiClO_4 -propylene carbonate, the most widely used electrolyte in lithium battery research. The additives studied were ten organic aromatic compounds including biphenyl, cyclohexylbenzene and hydrogenated diphenyleneoxide. For safety, focus was given to the overcharging tolerance of the lithium cells. Biphenyl is well-known as an overcharge protection additive. The purpose of this work was to find additives with a higher oxidation potential and longer charge–discharge cycle life than biphenyl. The oxidation potentials and currents of the additives were measured to determine whether or not these compounds work as overcharge protection additives. Charge–discharge cycling efficiencies were examined for lithium metal anodes. The results showed that cyclohexylbenzene and hydrogenated diphenyleneoxide have a higher oxidation potential and a higher lithium cycling efficiency than biphenyl.

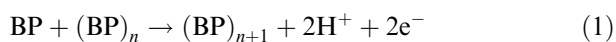
1. Introduction

Many commercial lithium ion cells are composed of lithium ion doped carbon anodes and LiCoO_2 cathodes with organic electrolyte solutions. They are generally charged to 4.2 V. Typical examples of electrolyte solutions generally used for lithium ion cells are LiPF_6 -mixed solvents of ethylene carbonate (EC), propylene carbonate (PC), diethyl carbonate (DEC), dimethyl carbonate (DMC) or methylethyl carbonate (MEC) [1]. They are widely used as high energy density power sources for cellular phones and personal computers. However, our previous abuse test results [2, 3] showed that the safety margin of these lithium ion cells was still too small for practical use and that they had two fundamental weaknesses: insufficient tolerance to overcharging and poor thermal stability. When overcharging and heating occur simultaneously, cell safety is greatly reduced. An example of a severe case is one in which there is high current overcharging. Some commercial lithium ion cells ignite and may explode with a 2 C rate overcharging with a high compliance charging voltage.

Nevertheless, there is a growing demand for an increase in the energy density of rechargeable cells. Rechargeable cells with lithium metal anodes are attractive because theoretically they have a higher energy density than lithium ion cells. However, the safety margin of these lithium metal cells, including their overcharging tolerance, is considerably smaller than that of lithium ion cells [4–9].

This paper describes the influence of electrolyte additives on safety and charge–discharge cycling life. The additives are designed to improve the overcharging tolerance of 4V-class cells with carbon or lithium metal anodes. Biphenyl (BP) [10–12] and 4,4'-dimethoxybiphenyl [13] have been investigated as examples of such additives. Ferrocene derivatives were studied as overcharge protection additives for 3V-class lithium cells such as Li/TiS_2 and Li/MnO_2 cells [14, 15]. However, they cannot be applied to 4V-class cells since their oxidation potentials are 3.2–3.6 V vs Li/Li^+ [14, 15]. BP has two aromatic rings and its oxidation potential (E_{ox}) (4.5 V vs Li/Li^+ [10]) is between the full cell charging voltage (4.2 V) for lithium ion cells and the voltage for complete lithium removal from lithium cobalt oxide cathodes ($\text{Li}_{0.5}\text{CoO}_2 \rightarrow \text{CoO}_2 + 0.5 \text{ Li}$, cell voltage: 4.3–4.6 V), which is lower than the E_{ox} of the electrolyte solutions generally used for lithium ion cells [1, 2, 16, 17]. Typical examples of solvents for these solutions are EC, PC, DEC, DMC or MEC [1]. LiPF_6 is widely used as the solute [1]. When 4V-class lithium cells are overcharged, BP is oxidized before the complete removal of the lithium from the lithium cobalt oxide cathodes and before electrolyte oxidation. This oxidation suppresses the chance of a hazardous event occurring. The oxidation of BP proceeds as shown in Equation 1 and produces poly-*p*-phenylene [10, 18]. BP is useful as a gassing agent since Equation 2 shows that electropolymerization during overcharging is accompanied by the rapid generation of H_2 gas [10, 18], which occurs on the

anodes. This behaviour assists the operation of the current cut device inside the cell by means of the internal pressure build-up [1, 2, 10, 11].



The additives we are looking for must have at least the two properties described below. First, the oxidation potential must be between the final standard full charging voltage (4.2 V vs C_6Li , 4.3 V vs Li/Li^+) and that of the complete removal of lithium from LiCoO_2 (4.3–4.7 V vs C_6Li , 4.4–4.8 V vs Li/Li^+), which is lower than those of electrolyte solutions generally used for lithium ion cells [1, 2, 10]. When the E_{ox} of the specified electrolyte solutions is lower than the voltage needed for complete lithium removal from the cathodes, the E_{ox} of the additives must be lower than those of the electrolyte

solutions. Secondly, the additives must not have a detrimental influence on the charge–discharge cycle life. In addition, the higher the oxidation reaction rate becomes, the better it should be in terms of ensuring the overcharge protection provided by the additives. Ten compounds as additives were tested. The chemical structures are shown in Figure 1 and Table 1. All the compounds except for hydrogenated diphenyleneoxide have π -electron conjugated aromatic rings. 1 M LiClO_4 –PC was used as the electrolyte solution – the most widely-used electrolyte solution for lithium cell research – to enable us to draw general conclusions solely about the influence of additives by avoiding the individual influences of the specified electrolyte solutions. Cycling efficiencies of the lithium metal anodes rather than the carbon anodes were measured for two reasons. (i) It is difficult to draw general conclusions about the influence of additives on the cycling performance of carbon anodes, because too many types of carbon are known [1]

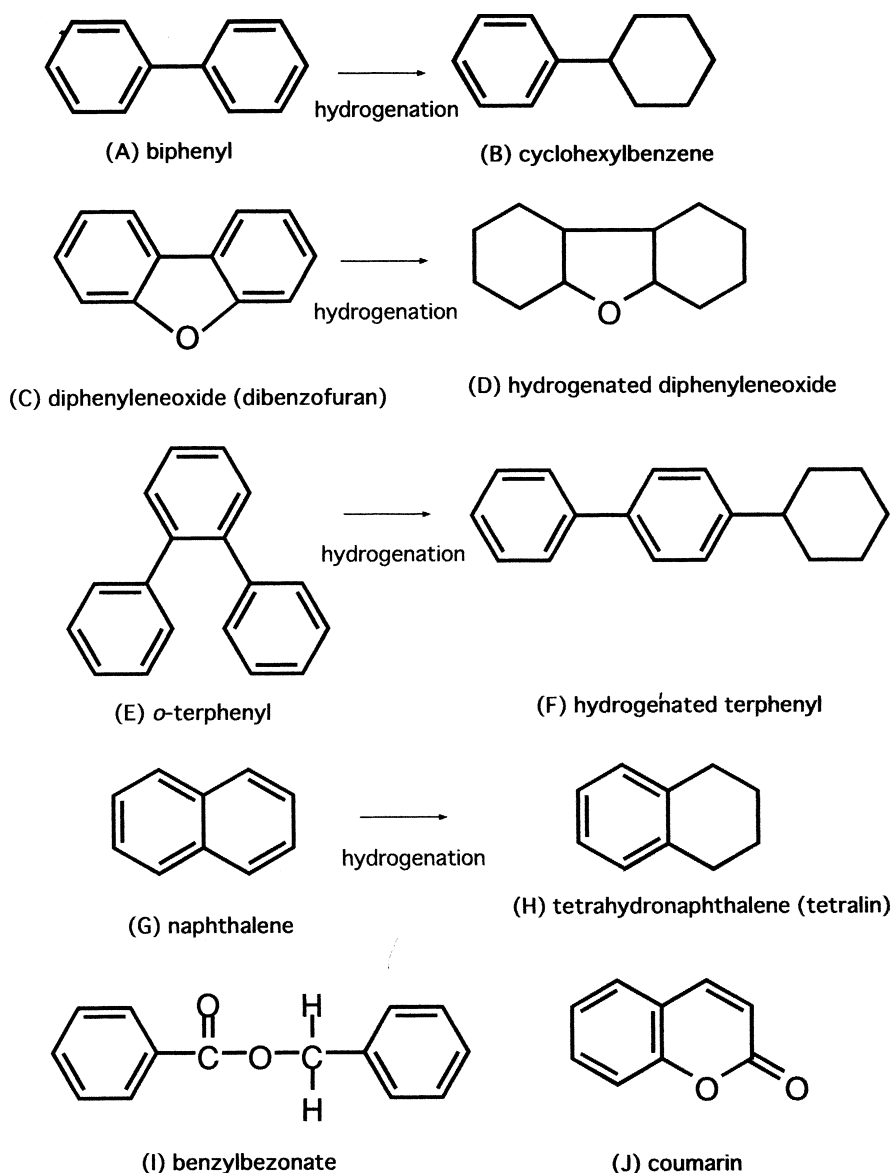


Fig. 1. Chemical structure of additives examined in this work.

Table 1. Number of aromatic rings of additives used in this study

Base compounds	Hydrogenated compounds	NAH/NA*
Biphenyl	cyclohexylbenzene	1/2
Diphenyleneoxide	hydrogenated diphenyleneoxide	2/2
<i>o</i> -Terphenyl	hydrogenated terphenyl	2/3
Naphthalene	tetrahydronaphthalene	1/2
Benzylbenzonate	—	—
Coumarin	—	—

*NAH: number of hydrogenated aromatic rings of base compounds,
 *NA: number of aromatic rings of base compounds.

and the influence of the electrolyte composition varies [1]. Each type of carbon should be tested independently for the proposed electrolyte systems when the cycle life of the specified carbon needs to be determined [1, 13]. (ii) The present technology level makes it difficult to fabricate lithium metal anodes with sufficient practical cycle life [4–9]. The influence of additives on cycle life should be determined more clearly for lithium metal anodes than for carbon anodes. Such effects are reported for some organic compounds, such as quinoneimine dyes [19] and pyromelic dianhydride [20], which produce lithium ion conductive protection film on a lithium anode as a result of reaction between the additives and lithium. Fundamentally, cells with carbon and lithium metal anodes both have problems of poor stability with regard to overcharging, although the overcharging tolerance of lithium metal cells is much smaller than that of carbon anode cells [4–9].

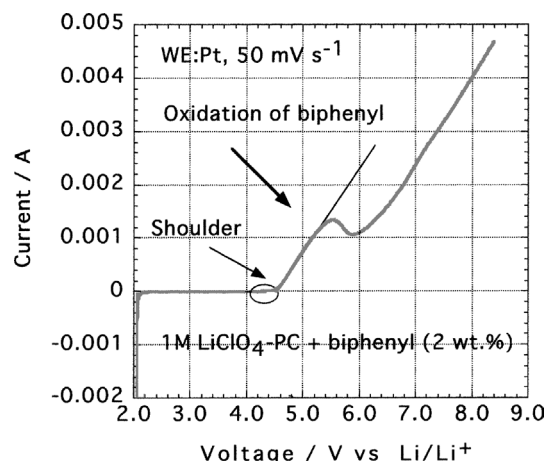
2. Experimental details

2.1. Electrolyte preparation

Test solutions were prepared by mixing the additives (Nippon Steel Chemicals Co.), which had been predried in a vacuum oven, and 1 M LiClO₄-PC solution (Tomiyama Pure Chemicals Co.) in an argon gas filled dry box (the H₂O and oxygen content was controlled at less than 1 ppm). The water content of the test solutions (determined by Karl–Fisher titration) was less than 20 ppm.

2.2. Oxidation potential measurements

The E_{ox} values of the additives or 1 M LiClO₄-PC were measured by potential linear sweep with a scan rate of 50 mV s⁻¹ at 25 °C, using a cylindrical glass test cell with a Li metal sheet counter electrode (0.1 mm thick) pressed on a Ni net (200 mesh, 15 mm long, 6 mm wide and 0.05 mm thick), a Pt sheet working electrode (4.5 mm long, 6 mm wide, 0.05 mm thick and 0.27 cm² in area) and a lithium reference electrode. LiCoO₂ working electrodes were prepared as a printed sheet (~150 μm thick) on an aluminium sheet (20 μm thick) by using poly(vinylidene fluoride) binder and conductive graphite carbon. E_{ox} values depend on how the shoulder in the voltage–current curves is treated [21, 22]. This shoulder is inevitable and does not disappear even at a low scan rate

Fig. 2. I/V curve for 1 M LiClO₄-PC + biphenyl at 25 °C.

of 1 mV s⁻¹. In this work E_{ox} values were determined as the voltage at the intersection of the x -axis base line (voltages) and a tangent of the rapid in the current curve. Figure 2 shows an example of the measurements for which the E_{ox} of BP in LiClO₄-PC is determined as 4.54 V vs Li/Li⁺. This value agrees with that measured for BP by using practical lithium ion cells [10, 11].

2.3. Lithium cycling efficiency measurements

Lithium charge–discharge cycling tests were carried out galvanostatically with the same cell as that used for the E_{ox} measurements at 25 °C. The charge–discharge cycling efficiency (Eff) was obtained from the ratio of the stripping charge (Q_s)/plating charge (Q_p) on the Pt electrode by using a 1.5 V potential vs Li/Li⁺ cut-off as the stripping (discharging) end point [23]. The charge–discharge current (I_{ps}) was 1.5 mA and the plating (charging) duration was 1 min (Q_p = 0.025 mAh).

2.4. Overcharging tests

Overcharging tests were carried out on commercially available prismatic lithium ion cells. These cells have an aluminium cell housing (can) or an aluminium-laminated package and have a cell capacity of around 600 mAh. They use LiCoO₂ cathodes and carbon anodes and liquid organic electrolytes or gel electrolytes (polymer matrix + liquid electrolytes). The latter cells are called ‘lithium ion polymer cells’. The electrolyte solutions for both cells are possibly LiPF₆-EC/DEC or EC/MEC, although the exact composition has not been provided by the battery manufacturers.

3. Results and discussion

3.1. Overcharging tests

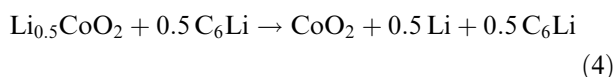
Lithium ion cells may be overcharged when the cell voltage is incorrectly detected by the charging control system, when the charger breaks down, or when the

wrong charger is used. There are three possible voltage–temperature patterns when a lithium ion cell is galvanostatically overcharged. A typical example of these patterns is shown in Figure 3 when a high compliance voltage, such as 10 V, is applied to fully charged cells (the cell voltage is generally 4.2 V). When the cells are overcharged, the lithium ions remaining in the lithium cobalt oxide cathode ($\text{Li}_{0.5}\text{CoO}_2$ after standard full charging) are removed at about 4.3 to 4.7 V and more lithium ions are supplied to the carbon anode than under standard charging conditions (Equations 3 and 4) [16, 17]. If the lithium insertion ability of the carbon anode is small, lithium metal may be deposited on the carbon, and this causes a serious reduction in thermal stability. After lithium has been removed from the cathode, the electrolyte starts to be oxidized. This electrochemical electrolyte oxidation results in a distinct heat output. When the cell temperature increases the electrolyte may simultaneously be reduced by the anode. When the overcharge current is low or the cells are thermally stable, the cell does not smoke as a result of the increase in impedance caused by electrolyte decomposition or separator shut-down. When the excess lithium deposition is large and dendritic lithium causes a soft short. In this case, the cell temperature does not increase and the cell may die without incident. A severe case of cell overcharging occurs when a high rate overcharging current is applied, such as a 2C rate, or the cell thermal stability is extremely low. In this case, the cell may smoke, ignite or explode.

Standard full charging



Overcharging



We performed overcharging tests galvanostatically on prismatic cells without a positive temperature coefficient (PTC) device, namely a current and thermal fuse, at 2C and a compliance voltage of 10 V, to investigate the overcharge tolerance of the cell itself. Two types of cell were tested. These were prismatic cells with an aluminium cell case and liquid electrolyte solution (cell A) and

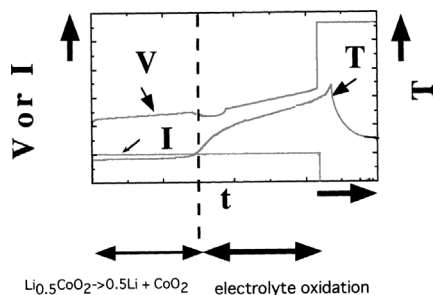


Fig. 3. Possible overcharging patterns: (*t*) charging time, (*T*) cell skin temperature, (*V*) cell voltage and (*I*) charging current.

lithium ion polymer cells with an aluminium-laminated package as the cell case and gel electrolyte (cell B). Before undertaking the abuse tests, we determined the charge capacities of the cells. The cells were discharged to 3.0 V at a 1C rate. Then, they were charged galvanostatically to 4.20 V at a rate of 0.5C, followed by constant voltage charging (4.2 V) for 5 h. The fully charged cell capacities of cell A and cell B were 640 and 620 mAh, respectively. Figures 4 and 5 show

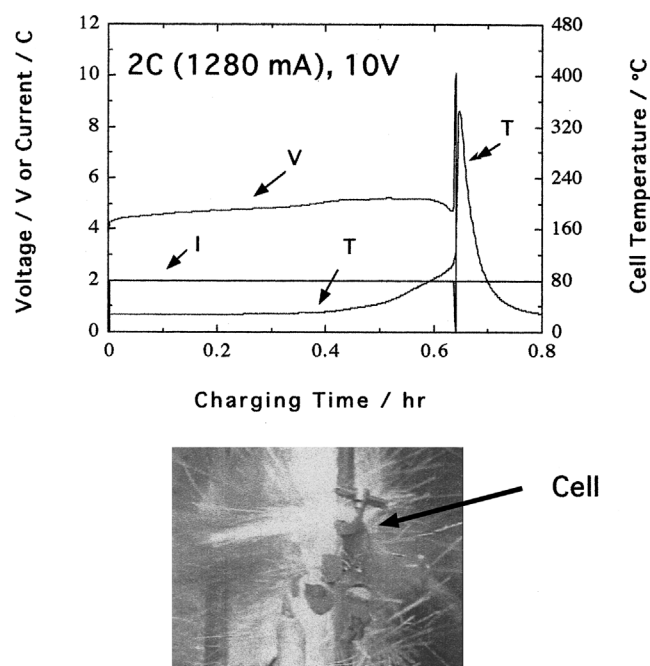


Fig. 4. Overcharging results for prismatic lithium ion cell (640 mAh).

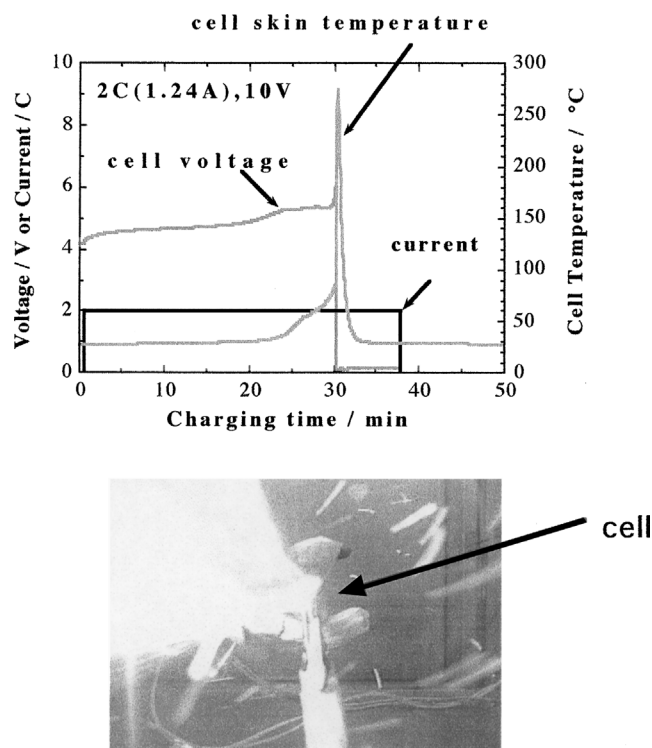


Fig. 5. Overcharging results for lithium ion polymer cell (620 mAh).

overcharging test results for cell A and cell B. Overcharging caused both cells to ignite and explode after the rapid cell temperature increase caused by electrolyte decomposition, which occurred after the complete removal of lithium from the lithium cobalt oxides.

No overcharging tests were carried out on the lithium metal cells because such cells are not commercially available. However, it is reported that AA-size cells that were on the market in 1987 with a lithium metal anode and a MoS_2 cathode (with an average discharge cell voltage of 1.9 V and a cell capacity of 800 mAh) [3–6] or prototype AA cells with an amorphous V_2O_5 cathode (with an average discharge voltage of 2.3 V and a cell capacity of 900 mAh) [7, 8] were capable of igniting at 0.3 to 1C overcharging with a compliance voltage of 10 V. These overcharging currents are lower than that of lithium ion cells (2C) [2, 3]. This means that both lithium ion cells and lithium metal cells suffer from the problem of a weak tolerance to overcharging.

3.2. Biphenyl

Figure 6 shows the E_{ox} measurement results for BP, compared with those for LiCoO_2 and PC obtained when using 1 M LiClO_4 -PC as the base-electrolyte. The E_{ox} values are with reference to Li/Li^+ . The measured E_{ox} is 2.90 V for LiCoO_2 , 4.54 V for BP and 6.01 V for PC. The measured E_{ox} (6.01 V) for 1 M LiClO_4 -PC is that for PC because the E_{ox} of LiClO_4 is higher than that of PC [21, 24]. The E_{ox} of BP is higher than that for the standard final charging voltage of carbon/ LiCoO_2 lithium ion cells (4.2 V vs C_6Li , about 4.3 V vs Li/Li^+), and lower than that of PC. These results mean that BP is oxidized after the full charging of a LiCoO_2 cell (a cathode composition of $\text{Li}_{0.5}\text{CoO}_2$) and before the beginning of the electrochemical electrolyte oxidation. This oxidation is an exothermic reaction and may lead to a large reduction in cell thermal stability (safety) when the cells are overcharged. We observed a black

deposit (poly-*p*-phenylene) on the Pt working electrode surface and gas generation (H_2) on the lithium counter electrode after the BP oxidation. These results agree with those reported in [10, 11].

Figure 7 shows the cycling efficiencies (Eff) of lithium metal anodes with or without BP in 1 M LiClO_4 -PC. When BP was added, the lithium cycling efficiency decreased greatly. This is because BP is easily reduced by alkali metals to form a one electron transferred stable reduction product, BP^- , Li^+ [25, 26]. BP^- , Li^+ is frequently utilized to study ion pairing states in non-aqueous solutions under dry and oxygen-free conditions [25, 26]. In addition, the solubility of BP^- , Li^+ in polar nonaqueous solutions is high [25, 26]. Large amounts of BP are consumed until an insoluble solid surface film is produced on the lithium anode. There is one difference between the effects of anode surface film formation on carbon anodes and lithium metal anodes. With carbon anodes, once the surface film is produced on the anode, it protects the reaction between the anode and electrolyte upon subsequent cycling. A protective film is easily formed on carbon anodes by the reaction between the anodes and the electrolyte [1]. Reactive additives such as vinylene carbonate are frequently used to form films quickly [1]. This is why BP can be used for commercial lithium ion cells despite its high reduction reactivity. However, with lithium metals, a pure lithium surface appears at every charging and the lithium is consumed as a result of the reduction of BP by Li at every cycle. Then, the discharge capacity decreases as the cycle number increases.

Our experimental results for both the oxidation potentials and lithium cycling efficiencies for BP can be summarized as follows. BP functions as an overcharging protection agent for lithium ion cells. However, with a lithium metal anode, the lithium cycling efficiency decreases greatly when BP is added. In addition, when a lithium ion cell is in a fully charged condition for a long period, there is concern about the adverse influence of BP on the cell storage life. This is because the E_{ox} of BP is close to the full charge voltage

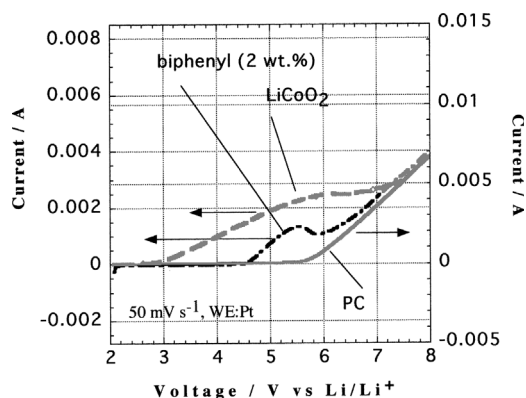


Fig. 6. I/V curves for biphenyl, LiCoO_2 and PC in 1 M LiClO_4 -PC at 25 °C.

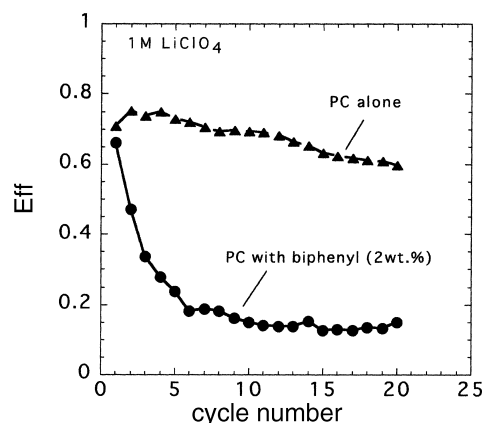


Fig. 7. Lithium cycling efficiencies (Eff) for 1 M LiClO_4 -PC with and without biphenyl, $I_{\text{ps}} = 1.5$ mA, $Q_{\text{p}} = 0.025$ mAh.

and there is an oxidation shoulder even at 4.3 V vs Li/Li⁺ (about 4.2 V vs C₆Li). This means the oxidation of BP may proceed gradually when a fully charged cell is stored for a long period.

We tested several compounds to find those expected to have better properties as overcharge protection additives than BP. These compounds must have higher E_{ox} values than BP. The reduction in lithium cycling efficiency must be less than with BP. It would also be advantageous if it were to improve the lithium cycling efficiency. A quicker oxidation rate would also be beneficial, which is detected via the rapid current increase in the I/V curves of the E_{ox} measurements, in order to guarantee overcharge protection.

3.3. Oxidation behavior of various compounds

The chemical structure of the additives examined here is shown in Figure 1. All the compounds except for hydrogenated diphenyleneoxide have aromatic rings. There are base compounds and their derivatives. The derivatives are compounds, in which one or two of the aromatic rings of the base compounds are hydrogenated, as summarized in Table 1. For example, cyclohexylbenzene is a BP derivative produced by the hydrogenation of one of BP's two aromatic rings.

Figure 8 shows the E_{ox} and the maximum current (I_{max}) in the I/V curves for 1 M LiClO₄-PC with additives (2 wt %). The I_{max} value reflects the oxidation rate. As seen in the comparison of the E_{ox} values and I_{max} values for three pairs of the base compounds/hydrogenated compounds (Figure 9); that is, biphenyl/cyclohexylbenzene, naphthalene/tetrahydronaphthalene and diphenyleneoxide/hydrogenated diphenyleneoxide, the hydrogenation of the aromatic rings results in an increase in the E_{ox} value and a decrease in the I_{max} value. The reason for these results is as follows. The more aromatic rings a compound has, the more π -electrons it has, and conjugated π -electrons are more easily oxidized than the σ -electrons of the stronger C-H single bonds of

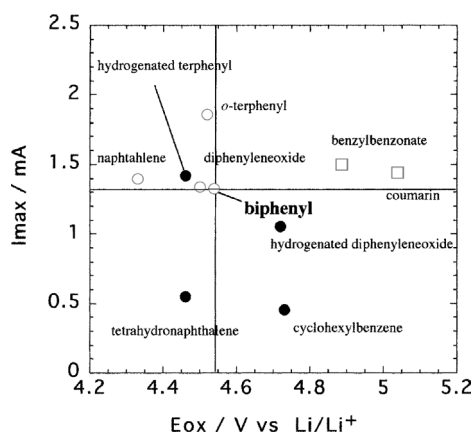


Fig. 8. Relationships between I_{max} and E_{ox} for 1 M LiClO₄-PC + additives (2 wt %).

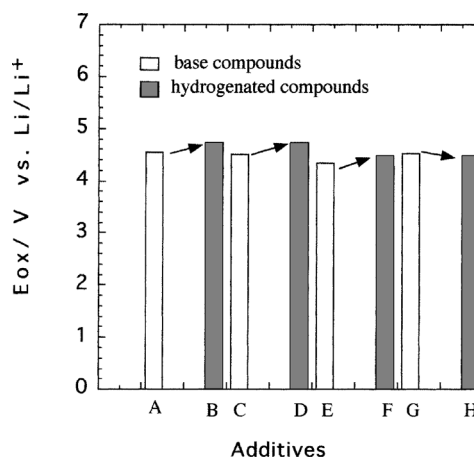


Fig. 9. E_{ox} values for 1 M LiClO₄-PC + additives (2 wt %). Key: (A) biphenyl, (B) cyclohexylbenzene, (C) diphenyleneoxide, (D) hydrogenated diphenyleneoxide, (E) naphthalene, (F) tetrahydronaphthalene, (G) *o*-terphenyl, and (H) hydrogenated terphenyl.

hydrogenated compounds. In hydrogenated diphenyleneoxide, two aromatic rings of diphenyleneoxide are completely hydrogenated. The difference between the E_{ox} values of these two compounds (diphenyleneoxide and hydrogenated diphenyleneoxide) is 0.22 V, which is larger than those for the pairs of biphenyl/cyclohexylbenzene (0.18 V) and naphthalene/tetrahydronaphthalene (0.13 V) in which just one of two aromatic rings of the base compounds is hydrogenated. Hydrogenated terphenyl does not have a higher E_{ox} value than *o*-terphenyl. This is considered to be due the difference in the chemical structure, because the hydrogenated terphenyl used here is not a derivative of *o*-terphenyl but of *p*-terphenyl.

Among the additives examined here, hydrogenated diphenyleneoxide, cyclohexylbenzene, benzylbenzotate and coumarin had higher E_{ox} values than BP. Benzylbenzotate and coumarin also had a higher I_{max} value. These two compounds have C=O bonds in the same way as PC, which also tends to have higher E_{ox} values in the same way as PC. However, the E_{ox} values of benzylbenzotate (5.04 V) and coumarin (4.88 V) are too high for the purpose of this work. These E_{ox} values are far beyond the voltage needed for the complete removal of lithium from LiCoO₂. Then, benzylbenzotate and coumarin do not protect the LiCoO₂ cells against overcharging hazards.

Although higher I_{max} values for *o*-terphenyl, hydrogenated terphenyl and naphthalene than that of BP were obtained, the E_{ox} values of these compounds were lower than that of BP. Therefore, it is difficult to use these compounds as overcharging protection additives and to eliminate the problems of BP, such as the cell capacity degradation that occurs with a long period of cell storage under fully charged conditions. Then, a comparison of the measured E_{ox} and I_{max} values with those of BP, showed that hydrogenated diphenyleneoxide and cyclohexylbenzene are, relatively speaking, the two best additives examined.

3.4. Cycling efficiency of lithium

Charge–discharge cycling tests were carried out on lithium metal anodes in 1 M LiClO₄–PC containing the overcharge protection additives. The cycling efficiency of lithium metal anodes in nonaqueous solutions cannot achieve 100% [27]. Cycling efficiency is affected by many factors including the reactivity of the electrolyte solution with lithium, lithium deposition morphology, cycling capacities, current densities, working electrode substrates, electrode stack pressure, operating temperatures and electrode orientation [23]. Here, the lithium cycling tests were performed with small amounts of lithium deposition, large amounts of electrolyte and without stack pressure. In this case, it has been proposed that one of the main reasons for the reduction in the lithium cycling efficiency is the formation of electrochemically inert lithium compounds (consumption of deposited lithium) resulting from the reaction between the solvent and the chemically reactive lithium freshly deposited just after charging [27]. If the reaction products produce Li⁺ ion conductive film, it may suppress the reduction of the electrolyte solutions by lithium during subsequent cycling. Aromatic ring compounds composed of C and H atoms, such as naphthalene, pyrene and anthracene, are reduced by lithium and form stable compounds of radical anions (one electron transfer products) and dianions (two electron transfer products). The subsequent deeper reduction leads to an irreversible reaction through the fission of aromatic rings and forms a surface film. This film formation is reported to suppress further reactions [19, 20, 28]. Lithium metal cells with these aromatic compounds as their cathodes are reported to have discharge capacity densities of 100–250 mAh g^{−1} per cathode weight and 1.10–1.57 V discharge voltages even though the solubility of these cathodes in LiClO₄–PC is very high [28]. This is considered to be the result of protective surface film formation [19, 20, 28].

Figure 10 shows the results of lithium charge–discharge cycling tests in 1 M LiClO₄–PC containing the overcharge protection compounds (2 wt %). Table 2 shows the average lithium cycling efficiency (Eff,av) from the 1st to the 20th cycles. All the compounds had higher efficiencies than BP. Cyclohexylbenzene and tetrahydronaphthalene exhibit higher efficiencies than PC, which means that these additives play a role in improving the lithium cycling efficiencies. Hydrogenated diphenyleneoxide shows only a slightly smaller Eff,av than PC. As seen in the comparison results for various base compound/hydrogenated compound pairs (Figure 11), the hydrogenation of aromatic rings results in an increase in the Eff,av values. The hydrogenated compounds show higher efficiencies due to a decrease in the reduction reactivity because the hydrogenated compounds were already reduced. Coumarin and benzylbenzonate with C=O bonds show a relatively lower efficiency because of their higher reactivity [27].

Figure 12 outlines the E_{ox} and Eff,av values. Summarizing these results, cyclohexylbenzene and hydrogenat-

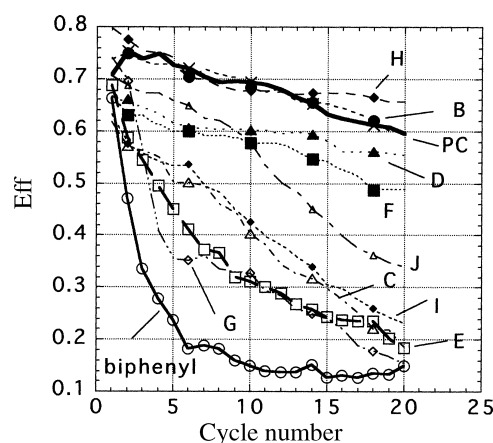


Fig. 10. Lithium cycling efficiencies (Eff) for 1 M LiClO₄–PC with additives (2 wt %), $I_{ps} = 1.5$ mA, $Q_p = 0.025$ mAh. Key: (B) cyclohexylbenzene, (C) diphenyleneoxide, (D) hydrogenated diphenyleneoxide, (E) *o*-terphenyl, (F) hydrogenated terphenyl, (G) naphthalene, (H) tetrahydronaphthalene, (I) benzylbenzonate, and (J) coumarin (Figure 1).

Table 2. Average lithium cycling efficiency (Eff,av) for 1 M LiClO₄–PC + additives (2 wt %)

Base compounds	Eff,av	Hydrogenated compounds	Eff,av
Biphenyl	0.211	cyclohexylbenzene	0.681
Diphenyleneoxide	0.397	hydrogenated diphenyleneoxide	0.600
<i>o</i> -Terphenyl	0.350	hydrogenated terphenyl	0.570
Naphthalene	0.335	tetrahydronaphthalene	0.697
Benzylbenzonate	0.416	–	–
Coumarin	0.535	–	–
No additive (PC alone)	0.678	–	–

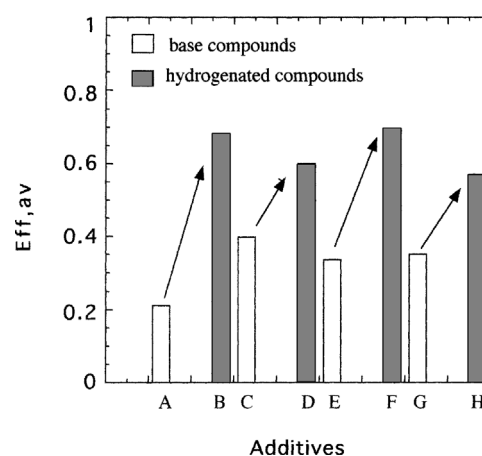


Fig. 11. Average lithium cycling efficiencies (Eff,av) for 1 M LiClO₄–PC + additives (2 wt %), $I_{ps} = 1.5$ mA, $Q_p = 0.025$ mAh. Key: (A) biphenyl, (B) cyclohexylbenzene, (C) diphenyleneoxide, (D) hydrogenated diphenyleneoxide, (E) naphthalene, (F) tetrahydronaphthalene, (G) *o*-terphenyl, and (H) hydrogenated terphenyl.

ed diphenyleneoxide exhibited higher E_{ox} and Eff values than BP with a minimum decrease in the Eff values compared with PC, and exhibited a slightly lower I_{max}

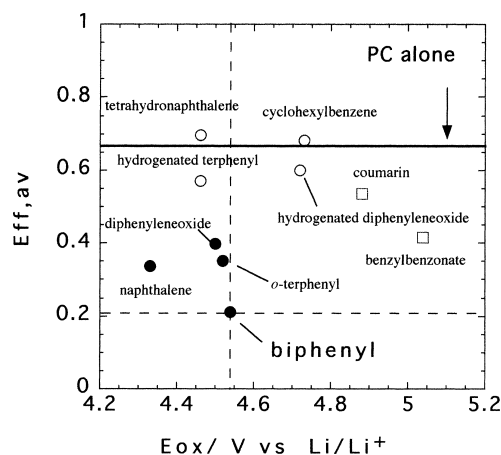


Fig. 12. Relationships between E_{ox} and Eff_{av} for 1 M $LiClO_4$ -PC + additives (2 wt %).

than BP. Coumarin and benzylbenzonate are inadequate as overcharge protection additives since these compounds had E_{ox} values that were too high and relatively low Eff values.

4. Conclusion

The influence of aromatic electrolyte additives on the safety and cycle life of lithium cells were examined. Cyclohexylbenzene and hydrogenated diphenyleneoxide provided better performance than biphenyl, in that they had a higher oxidation potential and a superior lithium cycling efficiency.

Lithium ion cells may now be used practically with the help of protective electronic circuits and devices to compensate for their poor tolerance to overcharging. The next step is to improve the safety even further to realize cells with a much higher energy density and also large practical cells for electric vehicles and electrically powered load leveling systems. At this stage, it is difficult to ensure the safety of such cells. Methods are required for guaranteeing the safety of the cell itself without the help of protective electronic circuits and devices.

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